



# Physicochemical properties of binder gel in alkali-activated fly ash/slag exposed to high temperatures



S.M. Park<sup>a</sup>, J.G. Jang<sup>a</sup>, N.K. Lee<sup>b</sup>, H.K. Lee<sup>a,\*</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, South Korea

<sup>b</sup> Structural Engineering Research Division, Korea Institute of Civil Engineering and Building Technology, 283 Goyangdae-ro, Ilsanseo-gu, Goyang 10223, South Korea

## ARTICLE INFO

### Article history:

Received 3 March 2016

29 July 2016

Accepted 9 August 2016

Available online xxxx

### Keywords:

Alkali activated cement (D)

Granulated blast-furnace slag (D)

Fly ash (D)

Temperature (A)

## ABSTRACT

The present study investigated the physicochemical properties of binder gel in alkali-activated fly ash/slag exposed to high temperatures. Strength test results showed that the strength increased until exposure to 400 °C and thereafter started to decrease. The strength increase below 400 °C was attributed to the binder gel which formed after exposure, decreasing the porosity. The dehydration of C-A-S-H and the formation of N-A-S-H simultaneously occurred, inducing the transformation of pore structure from microporous to mesoporous state. The crystallization of the binder gel resulted in an increase in the porosity, thereby inducing a decrease in the strength above 400 °C and is responsible for the transformation of the pore structure from mesoporous to macroporous state. The porosity under high temperatures had an inverse relationship with the strength, and was significantly altered as the binder gel underwent additional formation, dehydration and crystallization.

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## 1. Introduction

Fire can pose a threat to concrete structures due to the vulnerability of ordinary Portland cement (OPC) to decomposition at high temperatures. The main cause of a loss of strength in OPC exposed to high temperatures is the dehydration/dehydroxylation of calcium silicate hydrate (C-S-H) and portlandite ( $\text{Ca}(\text{OH})_2$ ) in the binder gel, and build-up of internal stress [1,2]. In particular, rehydration of dehydrated portlandite causes a serious damage by inducing expansion stresses [3], leading to spalling and cracking [1,2].

Alkali-activated cement has been the topic of numerous studies due to the superior performance of these materials at elevated temperatures, especially in relation to the use of geopolymer as a fire proof material [4] or the use of alkali-activated slag as an oil-well cement [5,6]. In particular, the thermal behavior of these materials is known to be less destructive in comparison to OPC [7]. A direct comparison of the performance capabilities at high temperatures was done in a study conducted by Gutiérrez et al., who reported a higher strength retaining capacity in alkali-activated slag as compared to OPC [8]. The performance of alkali-activated fly ash under high temperatures is reported to be remarkable as its ability to retain its structural integrity even surpasses that of alkali-activated slag [9]. However, the stability of this binder system is significantly dictated by the cation of the alkali silicate source ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ) and the alkali content ( $\text{SiO}_2/\text{Na}_2\text{O}$ ), i.e., potassium-based fly ash geopolymer tends to undergo less volumetric change during exposure

to heat in comparison to sodium-based fly ash geopolymer [10], and fly ash activated with a sodium hydroxide solution ( $\text{SiO}_2/\text{Na}_2\text{O} = 0$ ) shows greater dimensional stability in comparison to that activated with a sodium silicate solution ( $\text{SiO}_2/\text{Na}_2\text{O} > 0$ ) [11].

Recent studies are extensively focused on the alkali-activated binder system in a blend of both a calcium source (blast furnace slag) and an aluminosilicate source (fly ash or metakaolin) [12,13]. The chemistry of such a blended system can be found in earlier work [14,15]. The advantage of a blended system over the sole activation of fly ash or metakaolin is the potential for room-temperature fabricability as opposed to the high-temperature curing often required for the alkaline activation of fly ash or metakaolin [13,16]. Furthermore, the blended system possesses characteristics similar to those of both alkali-activated slag and alkali-activated fly ash; the blended system has higher chemical resistance in comparison with alkali-activated slag [17].

The mechanical properties of blended systems exposed to high temperatures have been explored by strength tests [18,19]. Alkali-activated slag/metakaolin blended concrete specimens presented residual strength of 14% after exposure to temperature of 600 °C, while the mortar specimens showed residual strength of 40% [18]. Specifically, the origin of the decline in the structural integrity was suggested to be a combination of dehydration of the reaction products and differences in the thermal expansion between the binder and the aggregates [18]. High volume fly ash cement is one that also showed superior thermal resistance in comparison to non-blended OPC [3]. Meanwhile, a detailed investigation of binder gel in blended systems exposed to high temperatures is not yet available. Only hypotheses can be drawn from the current understanding of the material in the effort to determine how

\* Corresponding author.

E-mail address: [haengki@kaist.ac.kr](mailto:haengki@kaist.ac.kr) (H.K. Lee).

calcium incorporation into an aluminosilicate binder degrades the mechanical performance at high temperatures, i.e., considering that the reaction pathway of the aluminosilicate precursor is significantly altered and that C-S-H hydrates, which are prone to dehydration, are instead or partially formed [19]. Consequently, no evidence with which to interpret the mechanical behavior of binder gel in a blended system, on which the interrelationship with the chemical characteristics can be established, exists. The present study therefore investigates the microstructure and chemistry of binder gel in alkali-activated fly ash/slag (AAFS) exposed to high temperatures.

## 2. Experimental procedure

### 2.1. Materials and sample preparation

The chemical compositions of the Class F fly ash and blast furnace slag used in this study are given in Table 1. Paste samples were synthesized by the alkaline activation of the fly ash and slag at a blend ratio of 1:1 by weight. The alkali-activator was produced from a mixture of a 4 M sodium hydroxide solution and a sodium silicate solution (Korean Industrial Standards KS Grade-3; SiO<sub>2</sub> = 29 wt%, Na<sub>2</sub>O = 10 wt%, H<sub>2</sub>O = 61 wt%, specific gravity = 1.38) at a weight ratio of 1:1 to reach a silicate modulus (SiO<sub>2</sub>/Na<sub>2</sub>O) of 1.44. The Na<sub>2</sub>O dosage was 4.1 g per 100 g of the solid (fly ash and slag) in each paste. The liquid to solid ratio was 0.4 by weight in all samples.

For the synthesis of the samples, a mixture of solid and liquid was mechanically stirred for 5 min at a room temperature and poured into a cubical mold 50 × 50 × 50 mm in size. All samples were demolded after 24 h and cured at a room temperature in a sealed condition for 28 days before exposure to the high-temperature conditions.

### 2.2. Test methods

At 28 days, the samples were placed in a furnace to be exposed to a temperature of 200, 400, 600 or 800 °C at a heating rate of 10 °C/min. The maximum temperature was preserved for 2 h so that the samples reached a state of thermal equilibrium [20,21]. The samples thereafter were slowly cooled to a room temperature inside the furnace before testing. Prior to the exposure step, the samples were dried at 100 °C for 2 h to remove any capillary water and to avoid the risk of spalling (thereby only accounting for the physicochemical changes of the binder gel) [20,21], while the reference sample was remained at an ambient temperature.

The physicochemical properties of the AAFS exposed to high temperatures were investigated by means of various analyses. Unconfined compressive strength tests, X-ray diffractometry (XRD), mercury intrusion porosimetry (MIP), pore size distribution analysis by the Brunauer, Emmett, Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) method, and solid-state <sup>29</sup>Si, <sup>27</sup>Al and <sup>23</sup>Na magic angle spin nuclear magnetic resonance (MAS NMR) spectroscopy were used. Samples were immersed in acetone and were desiccated for 24 h to arrest the reaction. Powdered samples passing a 64 μm sieve were used for XRD, BET/BJH, MAS NMR, while fractured samples were for MIP.

The unconfined compressive strength was conducted using a 500 kN universal testing machine with a loading rate of 0.02 mm/s, and the strength was averaged from five replicates of a respective sample. XRD was conducted using a SmartLab device manufactured by Rigaku with CuKα radiation at 40 kV and 30 mA and with a scan range of 5°

to 60° at a scan speed of 0.2°/min. Phase identification was performed using the International Centre for Diffraction Data (ICDD) PDF database. An Autopore VI 9500, manufactured by Micromeritics Instrument Corp., was used for the MIP tests in a pressure range of 0.2–413.7 MPa (30–60,000 psia). The BET surface area and BJH pore size distribution were determined by N<sub>2</sub> gas adsorption on an ASAP 2420 device, manufactured by Micromeritics Instrument Corp. Solid-state <sup>29</sup>Si, <sup>27</sup>Al and <sup>23</sup>Na MAS NMR spectroscopy were conducted using an INOVA 600 spectrometer (Agilent Technologies, U.S.A., at KBSI Western Seoul Center).

The solid-state <sup>29</sup>Si NMR spectra were collected at 119.182 MHz using a 5 mm HX-CPMAS probe, a 5 mm zirconia rotor and a spinning speed of 10.0 kHz. A pulse width of 2.2 μs and a relaxation delay of 22 s were employed. The chemical shifts were referenced to an external sample of tetrakis(trimethylsilyl)silane at –135.5 ppm with respect to TMS at 0 ppm. The solid-state <sup>27</sup>Al MAS NMR spectra were collected at 156.320 MHz using a 2.5 mm HX-CPMAS probe, a 2.5 mm low-Al zirconia rotor and a spinning speed of 22.0 kHz at an ambient temperature. A pulse width of 1.8 μs and a relaxation delay of 2 s were employed. The chemical shifts were referenced to an external sample of aqueous AlCl<sub>3</sub> at 0 ppm. The solid-state <sup>23</sup>Na MAS NMR spectra were collected at 158.700 MHz using a 2.5 mm diameter zirconia rotor and a spinning speed of 28.0 kHz at an ambient temperature. A pulse width of 1.3 μs and a relaxation delay of 10 s were employed. The chemical shifts were referenced to an external sample of aqueous NaCl at 0 ppm.

## 3. Results

### 3.1. Compressive strength

The compressive strength of AAFS exposed to high temperatures is shown in Fig. 1. The compressive strength gradually increased, reaching its highest value upon exposure temperature of 400 °C. The compressive strengths of the unexposed AAFS and those at 200 °C and 400 °C were 66.4, 106.9 and 122.9 MPa, respectively. The compressive strength of the samples exposed at a temperature of 600 °C was 96.4 MPa, clearly lower than when they were exposed to 400 °C, though still 45% higher than the initial strength. At 800 °C, the compressive strength was 50.2 MPa, i.e., 24% lower than the initial strength.

### 3.2. Crystalline phases

XRD patterns of the raw fly ash and slag are shown in Fig. 2. The raw fly ash contained peaks corresponding to unreactive crystalline phases quartz (SiO<sub>2</sub>, PDF #00-046-1045) and mullite (Al<sub>4-44</sub>Si<sub>1.56</sub>O<sub>9.78</sub>, PDF #01-074-4143), as well as an aluminosilicate amorphous hump at approximately 18–32° 2θ. The XRD pattern of the raw slag showed peaks which were assigned to anhydrite (CaSO<sub>4</sub>, PDF #01-072-0916), åkermanite (Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>, PDF #01-074-0990) and gehlenite

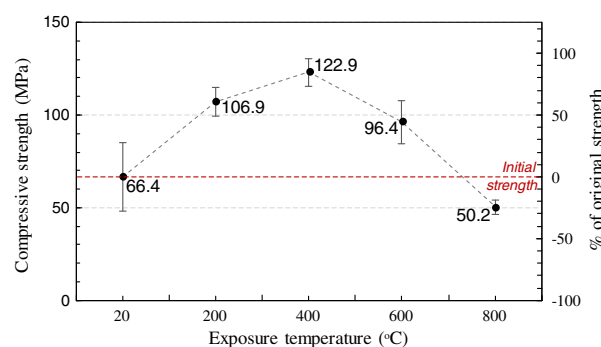


Fig. 1. Compressive strength of alkali-activated fly ash/slag exposed to high temperatures. Error bars indicate one standard deviation on either side of the mean.

Table 1  
Chemical composition of the fly ash and slag used in this study.

(wt%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	K <sub>2</sub> O	SO <sub>3</sub>	LOI <sup>a</sup>
Fly ash	57.0	21.0	10.0	4.8	1.3	1.5	1.5	1.4	1.0	2.71
Slag	32.4	11.5	0.6	47.7	3.0	0.6	0.5	0.5	2.7	0.29

<sup>a</sup> Loss on ignition.

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